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# The Production and Spectroscopy of Small Polyatomic Molecular Ions Isolated in Solid Neon

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## ABSTRACT

The use of a newly developed discharge sampling configuration has led to the stabilization of several small polyatomic molecular ions in solid neon in sufficient concentration for detection of their infrared absorptions. The results obtained in these experiments will be illustrated by observations of the ions which appear when carbon dioxide or oxygen is present in the system. In the experiments on carbon dioxide, the antisymmetric stretching absorptions of both  $\text{CO}_2^+$  and  $\text{CO}_2^-$  have been identified. An infrared absorption of  $\text{O}_4$  had previously been observed in systems in which an alkali metal atom, M, was codeposited with an Ar: $\text{O}_2$  mixture. The appearance of this absorption in the discharge sampling experiments on oxygen definitively excludes an alternate assignment of the absorption to an  $\text{MO}_4$  structure in which two  $\text{O}_2$  units are coordinated to a central alkali metal atom. Detailed isotopic substitution experiments support the assignment of four infrared absorptions to a vibrational fundamental and combination bands of  $\text{O}_4^+$ , for which no spectroscopic data have previously been reported. Analysis of the spectrum provides information regarding the molecular structure of  $\text{O}_4^+$ .

**Index Entries:** Cluster ions;  $\text{CO}_2^+$ ;  $\text{CO}_2^-$ ; infrared spectrum; matrix isolation; molecular ions; molecular structure; neon discharge;  $\text{O}_4^+$ ;  $\text{O}_4^-$ .

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## INTRODUCTION

Molecular ions are important in systems spanning the range from the terrestrial ionosphere to such industrial processes as chemical vapor deposition, microcircuit etching, and high-power laser-material interactions. There is a vast literature on their mass spectral detection. Photoelectron spectroscopy has also provided a very low resolution outline of the electronic energy levels of many small polyatomic cations. However, except for diatomic ions (1), a few simple polyatomic species (e.g.,  $\text{H}_3^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{OCS}^+$ ,  $\text{CS}_2^+$ , and  $\text{N}_2\text{O}^+$ ), and derivatives of acetylene and benzene, little is known about the details of molecular ion spectra (2-4). The determination of the infrared and optical spectra of molecular ions would greatly advance our knowledge of these species, since their structures and chemical-bonding properties could be derived from the spectral analysis. Moreover, these spectra would provide the basis for the development of sophisticated spectroscopic and laser-based techniques for remote sensing of specific ions, avoiding sampling problems inherent in the harsh environments associated with ion production.

The matrix isolation technique has proved to be a valuable adjunct to gas-phase studies of the spectra of molecular ions. In matrix isolation experiments, the molecular ion is trapped in dilute solid solution in argon or neon at 14 or 4 K, respectively. Under these conditions, atoms and electrons can undergo limited diffusion, but molecules are very effectively trapped. Sufficient concentrations of ions can often be stabilized for direct infrared or ultraviolet spectroscopic observation (5-7). The transparency of these matrix materials permits very broad spectral surveys—from the far infrared to the far vacuum ultraviolet. Argon matrix shifts for infrared absorptions of most covalently-bonded molecules and ions are less than 1%; neon matrix shifts are even smaller (3).

Among the most useful ion production techniques for matrix isolation sampling studies has been the codeposition with the sample of a beam of argon atoms that has been excited in a microwave discharge (5,6,8). Because excitation to the lowest energy levels of the argon atom, between 11.5 and 11.8 eV, predominates, this sampling configuration has been most useful for the study of halogen-containing molecular ions that can be formed in this energy range. The ionization potentials of many important ion precursors, including  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CO}_2$ , lie between 12 and 16 eV. Although the molecular cations of these species cannot be formed in significant concentration in the argon discharge system, they would be accessible in experiments using instead neon, for which the lowest excited energy levels lie between 16.6 and 16.8 eV. Such experiments, coupled with electron spin resonance (ESR) product detection, have been conducted by Knight (9), who has reported the stabilization of a number of important molecular ions and cluster ions. The infrared spectra of several small molecular ions formed in neon discharge sampling experiments are reported in this paper.

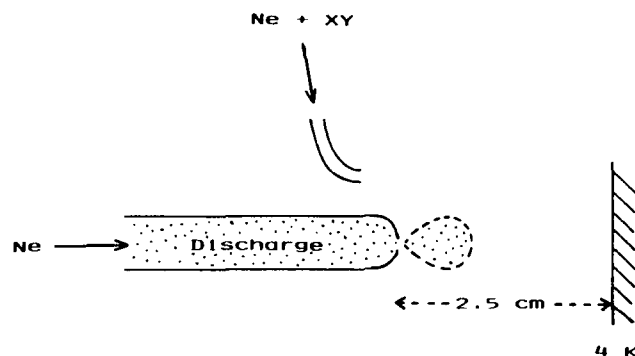


Fig. 1. Sampling configuration used in matrix isolation studies of the products of the interaction of discharge-excited neon atoms with the molecule XY.

### EXPERIMENTAL DETAILS\*

The carbon dioxide and oxygen (Matheson Co., Inc., E. Rutherford, NJ) and their isotopically substituted counterparts (Merck, Sharp, and Dohme Canada Ltd., Montreal, PQ, Canada), as well as the neon (Research Grade—Matheson Co., Inc., E. Rutherford, NJ and Spectra Gases, Inc., Irvington, NJ) used in these experiments, were not subjected to further purification, except for the condensation of the carbon dioxide at 77 K and pumping on the solid to remove relatively volatile trace impurities. Ne:CO<sub>2</sub> samples of mole ratio ranging from 200 to 500 and Ne:O<sub>2</sub> samples of mole ratio 100 and 200 were prepared using standard manometric procedures.

The discharge sampling configuration used for these experiments is illustrated in Fig. 1. A Vycor discharge tube was used, and 50 to 80 W output from a 2450 MHz microwave discharge was coupled into the flowing neon gas. The pinhole in the end of the discharge tube had a diameter of approximately 1 mm. The excited neon atoms and their resonance radiation interacted with the Ne:O<sub>2</sub> or Ne:CO<sub>2</sub> mixture, introduced outside the discharge region, over approximately 2.5 cm before the sample was frozen onto the nickel-plated copper laser mirror, affixed to the cold end of a Helitran (APD Cryogenics, Inc., Allentown, PA) continuous transfer liquid helium cryogenic cell maintained at approximately 4 K.

Absorption spectra of the resulting samples were obtained at a resolution of 0.2 cm<sup>-1</sup> between 600 and 4000 cm<sup>-1</sup> using a Bomem DA3.002 Fourier transform interferometer with a globar source, a KBr

\*Certain commercial instruments and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.

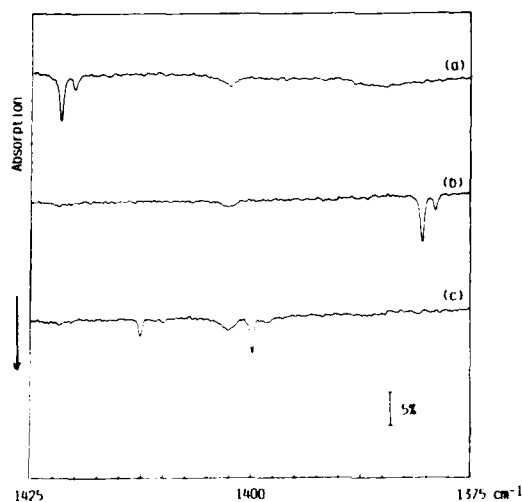


Fig. 2. (a) 3.21 mmol Ne:CO<sub>2</sub> = 400 codeposited over period of 176 min with 3.96 mmol discharged Ne. (b) 3.21 mmol Ne:CO<sub>2</sub> (90% <sup>13</sup>C) = 400 codeposited over period of 179 min with 3.74 mmol discharged Ne. (c) 5.78 mmol Ne:CO<sub>2</sub> (91.5% <sup>18</sup>O) = 500 codeposited over period of 219 min with 4.71 mmol discharged Ne.

beamsplitter, transfer optics which have previously been described (10), and a HgCdTe detector cooled to 77 K. After the infrared spectrum of the initial deposit had been recorded, further information was obtained by studying the spectra which resulted upon irradiation of the sample by the full or filtered output of a medium-pressure mercury arc. Corning filters of glass types 3384, 3389, 3391, and 7380, with short wavelength cutoffs at 490, 420, 400, and 345 nm, respectively, were used.

## RESULTS AND DISCUSSION

Because CO<sub>2</sub> has the relatively high ionization potential of 13.77 eV (11) and because the gas-phase band center of the  $\nu_3$  absorption of ground-state CO<sub>2</sub> has been reported (12), the interaction of excited neon atoms and their resonance radiation with CO<sub>2</sub> was chosen as a test of the procedure. Very strong absorptions of CO<sub>2</sub> were present in the spectrum of the deposit. In addition, as is shown in trace (a) of Fig. 2, an absorption appeared at 1421.7 cm<sup>-1</sup>, with a satellite at 1420.1 cm<sup>-1</sup>. Since the more prominent peak is shifted from the gas-phase CO<sub>2</sub> band center, at 1423.08 cm<sup>-1</sup>, by only 1.4 cm<sup>-1</sup>, its assignment to CO<sub>2</sub> is suggested. Support for this assignment is obtained from isotopic substitution experiments. In the study of a CO<sub>2</sub> sample with 90% carbon-13 enrichment, shown in trace (b) of Fig. 2, the more prominent peak of the absorption pair appeared at 1380.4 cm<sup>-1</sup>. The observed isotopic shift, 41.3 cm<sup>-1</sup>, can be compared with the calculated value (13) of 40.5 cm<sup>-1</sup> for a linear OCO structure. As is shown in trace (c) of Fig. 2, when a CO<sub>2</sub> sample enriched to 91.5% in oxygen-18 was used, the most prominent peak appeared at

1399.8  $\text{cm}^{-1}$ . The observed isotopic shift of 21.9  $\text{cm}^{-1}$  can be compared with a calculated shift of 21.8  $\text{cm}^{-1}$  for  $\text{C}^{18}\text{O}_2$ . Furthermore, a weaker peak at 1412.4  $\text{cm}^{-1}$ , 9.3  $\text{cm}^{-1}$  below the 1421.7  $\text{cm}^{-1}$  peak, can reasonably be assigned to  $^{16}\text{OC}^{18}\text{O}$ .

Common to all three traces of Fig. 2 is a weak, broad absorption at 1402.4  $\text{cm}^{-1}$ . This peak has also been observed in preliminary studies of the interaction of excited neon atoms and their resonance radiation with  $\text{H}_2\text{O}$ . Since the gas-phase band center of the bending fundamental of ground-state  $\text{H}_2\text{O}$  has been determined from emission studies (14,15) and high resolution photoelectron spectroscopy (16) to lie at 1408.4  $\text{cm}^{-1}$ , this band is tentatively assigned to  $\text{H}_2\text{O}$ .

In order to prevent the rapid buildup of a large electric field, which would repel cations from the surface of the deposit, negatively-charged species must also be trapped in the solid, giving overall charge neutrality. As in the experiments of Knight (9), species such as  $\text{O}_2^-$  and  $\text{OH}^-$ , formed from water and other trace impurities in the system, may contribute to the anion population. A prominent, structured absorption appeared in these experiments at 1658.3  $\text{cm}^{-1}$ . The  $\nu_3$  absorption of  $\text{CO}_2$  has been identified by Hisatsune and coworkers (17,18) at 1671  $\text{cm}^{-1}$  in studies of the infrared spectra of gamma-irradiated sodium formate pressed in alkali halide disks. Jacox and Milligan (19) first reported a complicated pattern of absorptions between approximately 1585 and 1630  $\text{cm}^{-1}$  with isotopic substitution behavior appropriate for assignment to  $\text{CO}_2$  when a beam of alkali metal atoms was codeposited with an Ar:  $\text{CO}_2$  sample. Subsequent rare-gas matrix studies in the laboratories of Margrave (20-22), Bencivenni (23,24), and Perchard (25) have provided more details regarding the properties of the  $\text{M}^+\text{CO}_2^-$  species. Calculations by Jordan (26,27) have suggested that the alkali metal cation is coordinated in a cyclic structure with the two oxygen atoms of the bent  $\text{CO}_2$  moiety, consistent with the observed dependence of the positions of the absorptions on the nature of the alkali metal. For  $\text{CO}_2$  with a valence angle of 135 degrees, the calculated (13) carbon-13 isotopic shift in the 1658.3  $\text{cm}^{-1}$  peak is 45.0  $\text{cm}^{-1}$ , compared with an observed shift of 44.2  $\text{cm}^{-1}$ . The calculated shift of 28.4  $\text{cm}^{-1}$  for  $\text{C}^{18}\text{O}_2$  may be compared with an observed shift of 27.7  $\text{cm}^{-1}$ . An intermediate peak, shifted by 13.2  $\text{cm}^{-1}$  from the 1658.3  $\text{cm}^{-1}$  absorption, is appropriate for assignment to  $^{16}\text{OC}^{18}\text{O}$ .

When the deposit was exposed to mercury-arc radiation of a wavelength longer than 490 nm for a few minutes, the 1658.3  $\text{cm}^{-1}$  absorption was destroyed, and the 1421.7  $\text{cm}^{-1}$  absorption decreased in intensity. A weak to moderately intense peak at 1241.5  $\text{cm}^{-1}$ , attributable to  $\text{NO}_2$  isolated in a neon matrix (28), grew somewhat. These observations could be explained if electron detachment from  $\text{CO}_2^-$  occurred, followed by recombination of the resulting electrons either with  $\text{CO}_2$  or with a trace impurity of  $\text{NO}_2$  formed in the discharge.

In the Ne:  $\text{CO}_2$  experiments, weak absorptions often appeared at 1164.4 and 1320.3  $\text{cm}^{-1}$ . As shown in trace (a) of Fig. 3, when a Ne:  $\text{O}_2$  = 200 sample was codeposited with a beam of excited neon atoms, these

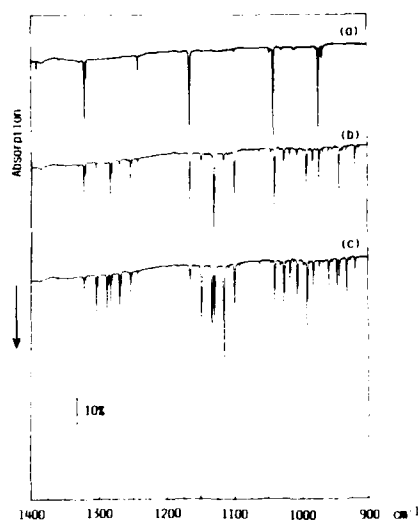


Fig. 3. (a) 4.17 mmol  $\text{Ne}:\text{O}_2 =$  codeposited over period of 183 min with 5.13 mmol discharged Ne. (b) 4.60 mmol  $\text{Ne}:\text{}^{16}\text{O}_2:\text{O}_2$  (93%  $^{18}\text{O}$ ) = 200:1:1 codeposited over period of 240 min with 6.85 mmol discharged Ne. (c) 6.47 mmol  $\text{Ne}:\text{O}_2$  (57.8%  $^{18}\text{O}$ ) = 100 codeposited over period of 287 min with 8.88 mmol discharged Ne.

two absorptions became prominent. Other prominent absorptions appeared at 973.1 and 1039.9  $\text{cm}^{-1}$  in the  $\text{Ne}:\text{O}_2$  studies. A moderately strong absorption at 796.3  $\text{cm}^{-1}$  and weak absorptions at 2808.5 and 2948.6  $\text{cm}^{-1}$  were also characteristic of this system. (In trace (a), the absorptions at 1241.5 and 1391.6  $\text{cm}^{-1}$  can be assigned to small concentrations of  $\text{NO}_2$  and  $\text{HO}_2$  (29), respectively.) These new absorptions were unshifted when a small concentration of  $\text{H}_2$ ,  $\text{D}_2$ , or  $\text{NO}$  was added to the discharged Ne sample, suggesting that the species responsible for them do not contain hydrogen or possess nitrogen-oxygen bonds. The much greater prominence of the 1164.4 and 1320.3  $\text{cm}^{-1}$  bands in the  $\text{Ne}:\text{O}_2$  experiments than in the  $\text{Ne}:\text{CO}_2$  experiments also indicates that the species that contributes them does not possess carbon-oxygen bonds.

When a  $\text{Ne}:\text{O}_2 = 100$  sample with 57.8% random enrichment in oxygen-18 was codeposited with excited neon atoms, the spectrum shown in trace (c) of Fig. 3 was obtained. Each of the product absorptions of the spectrum of trace (a) (excepting the  $\text{HO}_2$  and  $\text{NO}_2$  peaks) was replaced by six absorptions, indicating that the carrier of each absorption possesses three or more oxygen atoms. The positions of the isotopically substituted counterparts of the 1039.9  $\text{cm}^{-1}$  absorption correspond with those reported by Andrews and Spiker (30) for  $\text{O}_3$  isolated in an argon matrix, with only a small, constant matrix shift. However, the intensity pattern indicates a relative depletion in  $^{18}\text{O}_3$  and  $^{18}\text{O}^{16}\text{O}^{18}\text{O}$ . The isotopic shifts for the absorption at 796.3  $\text{cm}^{-1}$  also correspond well with those reported by Jacox and Milligan (31) for the  $\nu_3$  fundamental of  $\text{O}_3$ , formed in the earlier work in the presence of an alkali metal cation. However, as

for  $O_3$ , the intensities of the two peaks contributed by species with oxygen-18 in both end positions are considerably lower than would be expected for random oxygen-18 enrichment. This anomaly can be explained by postulating that oxygen atoms formed from trace  $^{16}O_2$  and water impurity in the discharge tube react with oxygen-18 enriched  $O_2$  outside the discharge region. As in many other discharge sampling experiments using a similar configuration, the oxygen-18 enriched sample is almost completely excluded from the discharge region. On the other hand, the isotopic intensity distributions observed for the groups of peaks associated with the absorptions at 973.1, 1164.4, 1302.3, 2808.5, and 2948.6  $cm^{-1}$  do not show an intensity depletion for the fully oxygen-18 substituted product, suggesting a different mechanism for the formation of these species.

In order to obtain further information regarding the carriers of these peaks, the experiment shown in trace (b) of Fig. 3, using a  $Ne: ^{16}O_2: O_2$  (93%  $^{18}O$ ) = 200:1:1 sample, was conducted. Consistent with the exclusion of the neon-oxygen mixture from the discharge region, only the peaks corresponding to  $^{16}O_3$  and  $^{16}O^{18}O^{18}O$  and to their negatively-charged counterparts were prominent in the spectra of  $O_3$  and  $O_3^-$ . On the other hand, each of the remaining absorptions of the isotopically unsubstituted sample was replaced with a group of three absorptions, with the central peak more prominent than the two end peaks. This behavior indicates that two symmetrically equivalent  $O_2$  units are present in the species that contribute these absorptions.

Studies of the photolysis of the deposit by filtered mercury-arc radiation have provided further clues to the identification of the product species. The photodissociation threshold for the unidentified product absorptions was observed between 420 and 490 nm. Near the photodissociation threshold, the 973.1  $cm^{-1}$  peak and its isotopically-substituted counterparts disappeared more slowly than the remaining peaks. On the other hand, when a short wavelength cutoff of 345 nm was used for the photolysis, the 973.1  $cm^{-1}$  group of peaks disappeared more rapidly than the other peaks.

The determination that the 973.1  $cm^{-1}$  peak possesses two symmetrically equivalent  $O_2$  units and that no other absorptions in the spectrum are associated with this product suggests that it may be contributed by  $O_4$ . When relatively concentrated  $Ar:O_2$  samples are codeposited with a beam of alkali metal atoms, an absorption appears near 1000  $cm^{-1}$  (32-34). Although the species responsible for this absorption was at first thought to possess an  $MO_4$  structure that has two equivalent  $O_2$  units coordinated with a central alkali metal atom (32,33), Jacox and Milligan (34) proposed that the absorption might instead be contributed by  $M^+O_4$ , with the trans- $O_4$  structure calculated by Conway (35). Subsequent Raman studies by Smardzewski and Andrews (36) led to the assignment of the central oxygen-atom stretching absorption near 300  $cm^{-1}$ , consistent with the trans- $O_4$  structure. However, lingering doubt remained. Although in principle random oxygen-18 isotopic substitution should lead to the appearance of 10 oxygen-isotopic species of trans- $O_4$ , only six



peaks have been observed. The normal coordinate calculations by Jacox and Milligan for the Conway structure showed that, because of frequency coincidences, only six peaks should appear. The peak separations in the present experiments closely parallel those reported in the alkali metal experiments. The relative intensities of the individual peaks are also consistent with those calculated taking into account the frequency coincidences, further supporting the assignment.

The remaining absorptions appear with the same relative intensities in all of the experiments, suggesting that they are contributed by a single species. As has been noted, the isotopic pattern of trace (b) of Fig. 3 dictates that this product possess two equivalent  $O_2$  units. The identification of  $O_3$  and  $O_4$  requires that one or more cation species be present in order to preserve overall charge neutrality of the deposit and strongly suggests that  $O_2$ , with an ionization potential of 12.07 eV (37), is the electron source, leading to the stabilization of  $O_2^-$  in the system. The mass spectrometric studies of Yang and Conway (38) demonstrated that the reaction of  $O_2$  with  $O_2^-$  to form  $O_4^-$  is exothermic by approximately 10 kcal/mol (42 kJ/mol). Hiraoka (39) has summarized more recent studies of this species and has revised the exothermicity of the above reaction to  $9.15 \pm 0.50$  kcal/mol ( $38.3 \pm 2.1$  kJ/mol), slightly less than the value of  $10.49 \pm 0.50$  kcal/mol ( $43.9 \pm 2.1$  kJ/mol), which he found for the corresponding reaction of  $O_2$ . Knight (9) has identified the electron spin resonance spectra of several dimer cations in analogous experiments. Since clustering of  $O_2$  with  $O_2^-$  to form  $O_4^-$  has been observed in these experiments, it appears reasonable to propose that the unassigned infrared absorptions might be contributed by  $O_4^-$  formed in the analogous cation-molecule reaction.

Extremely little is known about the structure of  $O_4^-$ . The INDO calculation of Conway (35) suggested that this species should have a planar trans- structure very similar to that of  $O_4$ . The isotopic shift and intensity pattern of the  $1164.4\text{ cm}^{-1}$  group of absorptions closely follows that of the  $973.1\text{ cm}^{-1}$  group of absorptions, assigned to trans- $O_4$ , consistent with the assignment of the  $1164.4\text{ cm}^{-1}$  group to the same fundamental of trans- $O_4^-$ . Although many other  $O_4$  structures can be envisioned, only the linear or the planar trans- structure could give the observed isotopic distribution. The isotopic shift and intensity pattern of the  $1320.3\text{ cm}^{-1}$  group of absorptions is similar to the  $973.1$  and  $1164.4\text{ cm}^{-1}$  groups. Since only the  $\nu_5(b_u)$  fundamentals of trans- $O_4^-$  and trans- $O_4$  should have this pattern, the  $1320.3\text{ cm}^{-1}$  group of peaks may be contributed by a combination with an  $O_4^-$  fundamental near  $150\text{ cm}^{-1}$  which possesses  $a_g$  symmetry, for which the isotopic shifts would be sufficiently small that the overall pattern would be dominated by the  $\nu_5$  contribution. Alternatively, the  $\nu_5$  fundamental of  $O_4^-$  may interact strongly with a combination of several very low frequency fundamentals that possesses overall  $b_u$  symmetry. Normal coordinate calculations for the trans- $O_4^-$  and trans- $O_4$  structures suggest that the infrared-inactive  $\nu_1$  fundamental of these two species, involving the in-phase stretching of the two  $O_2$  units, should lie at a higher frequency than the corresponding

out-of-phase stretching fundamental ( $\nu_5$ ). This suggests the assignment of the weak  $2808.5\text{ cm}^{-1}$  absorption to the  $\nu_1 + \nu_5$  combination band of trans- $\text{O}_4^-$ , giving a value of  $1644.1\text{ cm}^{-1}$  for  $\nu_1$ . The  $2948.6\text{ cm}^{-1}$  absorption might then be assigned to the combination band resulting from the addition of  $\nu_1$  to the group of vibrations which contributes the  $1320.3\text{ cm}^{-1}$  absorption.

## CONCLUSIONS

Upon codeposition of a Ne:CO<sub>2</sub> sample with a beam of neon atoms excited in a microwave discharge, a sufficient concentration of CO<sub>2</sub><sup>-</sup> is stabilized for detection of its  $\nu_3$  absorption at  $1421.7\text{ cm}^{-1}$ , very near the gas-phase band center. An absorption at  $1658.3\text{ cm}^{-1}$  in this system has isotopic substitution behavior appropriate for its assignment to  $\nu_3$  of CO<sub>2</sub><sup>-</sup>. When a Ne:O<sub>2</sub> sample is codeposited with a beam of excited neon atoms, absorptions of O<sub>3</sub><sup>-</sup>, O<sub>3</sub><sup>-</sup>, O<sub>4</sub><sup>-</sup>, and O<sub>4</sub><sup>-</sup> are identified. Isotopic substitution experiments indicate that the O atoms which react produce the O<sub>3</sub><sup>-</sup> species are formed from oxygen-containing impurities in the discharge region. The correspondence of the O<sub>4</sub><sup>-</sup> absorption with that previously reported in systems in which an alkali metal was present definitively excludes the alternate assignment of the absorption to an MO<sub>4</sub> structure in which two O<sub>2</sub> units are coordinated to a central alkali metal atom. The isotopic substitution experiments also support a planar trans-structure for both O<sub>3</sub><sup>-</sup> and O<sub>4</sub><sup>-</sup>. The  $1164.4\text{ cm}^{-1}$  absorption is assigned to  $\nu_5$  ( $b_{1g}$ ) of trans-O<sub>4</sub><sup>-</sup> and three higher frequency absorptions to combination bands of this species.

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